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# Ammonia, Methane and Hydrogen for Gas Turbines

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**Abstract**

Ammonia has been identified as a sustainable fuel for transport and power applications. Similar to hydrogen, ammonia is a synthetic product that can be obtained either from fossil fuels, biomass or other renewable sources. Since the 1960's, considerable research has taken place to develop systems capable of burning the material in gas turbines. However, it is not until recently, that interest in ammonia has regained some momentum in the energy agenda as it is a carbon free carrier and offers an energy density higher than compressed hydrogen. . Therefore, this work examines combustion stability and emissions from gaseous ammonia blended with methane or hydrogen in gas turbines. Experiments were carried out in a High Pressure Combustion Rig under atmospheric conditions employing a bespoke generic swirl burner. OH* Chemiluminescense was used for all trials to determine reactivity of the radical. Emissions were measured and correlated to equilibrium calculations using GASEQ. Results show that efficient combustion can be achieved with high power but at very narrow equivalence ratios using both hydrogen and methane blends. Moreover, low concentrations of OH radicals are observed at high hydrogen content, probably as a consequence of the high $NH_2$ production.


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*Keywords: Ammonia; Hydrogen; Stability; Gas Turbines.*

## 1. Introduction

Fuel flexibility is one of the major areas of investigation for gas turbines research. Sources that can produce minimal or zero $CO_2$ , are currently being investigated by various groups, with the goal of identifying; clean sources with high power output and low emissions to cope with energy demand, whilst reducing climate change. Ammonia has been considered as a potential candidate for many years and is more cost effective than pure hydrogen. Ahlgren [1] performed a study where he compared the fuel power density F (a unit that takes into consideration the power in the fuel and the energy required to transport it in pipelines) for different fuels. He concluded that ammonia and methanol are the best renewable fuels options if compared with pure hydrogen. However, there is still very little literature describing ammonia in complex flows such as those used in gas turbines.

Karabeyoglu et al. [2] present some important issues on the use of ammonia, arguing that toxicity and low energy density are the key issues. They also report the development of technologies to burn $NH_3$ in gas turbines with the objective of minimizing NOx and $NH_3$ emissions in the flue gases. However, most

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of these technologies are still in their early stages. Grcar et al. [3] combined experimental and modelling investigation of ammonia chemistry in a hot combustion environment that was below adiabatic flame temperatures. The research concluded that the final products of $NH_3$ oxidation remained sensitive to mixing even at temperatures below those of self-sustaining flames. At low temperatures, $NH_3$oxidation occurred in a premixed reaction zone, but at sufficiently high temperatures, a non-premixed reaction zone that produces significantly less NO than the equivalent premixed system might develop.

SPG Advanced Propulsion and Energy [4] gives a coherent history of the use of ammonia in turbojet systems and Solar used a 250HP T-350 single can burner to run experiments in the 1960's. Performance of the engine using ammonia was comparable to that with JP-4, where ammonia at 2.35 times the quantity of hydrocarbon fuels provided cooler turbine inlet temperatures.

Pratt [5] and Verkamp et al. [6] have shown that the partial cracking of ammonia into hydrogen and NH is also beneficial, as this blend approximates the properties and burning velocities of methane and propane, thus providing better efficiencies, higher stability, lower NOx and high levels of power.

Iowa State University [7] have designed a system capable of producing 40kW of power, with nozzles, swirl stabilisers and a self-sustained heat exchanger similar to those employed in gas turbines. The group found that the use of a flame holder increased the efficiency of the combustion process, with a clear reduction of NOx emissions due to the recirculation of the molecule and its interaction with the amines in the dissociated molecules.

Although there have been developments in this area, further tests are still required to produce a stable, high power gas turbine capable of producing energy at an industrial scale using ammonia with hydrogen and/or methane. Therefore, this work is focused on looking at different blends of fuel in a generic swirl burner relevant to industrial systems. Numerical and experimental analyses were performed in order to provide enough data for future works for close-to-industrial prototypes.

## 2. Setup

### *2.1. Experimental trials*

Experiments were performed at the Gas Turbine Research Centre (GTRC). The GTRC is a facility which consists of two major combustion rigs each designed for detailed investigation of combustion and emissions characteristics at representative gas turbine conditions. One of these rigs, the High Pressure Combustion Rig (HPCR) can perform at pressures up to 16bara and deliver air at 5 kg/s at temperatures reaching 900K. For this project a High Pressure Optical Chamber (HPOC) was fitted with a generic lean pre-mixed swirl burner, Fig. 1. Quartz windows allocated at both sides of the combustion chamber and in the exhaust duct allow the burner exit to be viewed from both axial and radial positions. A tangential swirl burner, relevant to Siemens devices, was designed based on previous experience and numerical models from past projects.

The GTRC has a unique gas mixing facility that can blend up to five gas streams by mass, in real time, enabling the effect of variations in fuel compositions on the combustion process to be investigated. Coriolis mass flow meters are used on the fuel and air lines allowing the accurate control of equivalence ratio, Re numbers and ammonia/methane/hydrogen concentrations.

OH* chemiluminescense measurements were taken on atmospheric $CH_4$, $NH_3$ -$H_2$ and $CH_4$ -$NH_3$ swirl flames. The chemiluminescense intensity of the OH radical is low and requires the use of an image intensifier to capture the light emitted in the UV range. A Dantec Dynamics Hi Sense Mk II CCD camera with a 1.3 megapixel resolution was coupled to a Hamamatsu C9546-03L image intensifier was used. A specialty 78 mm focal length lens (F-stop = f/3.8) capable of capturing light in the UV wavelength range was installed on the image intensifier along with a narrow band pass filter centered at 307 nm (FWHM = 10 nm).

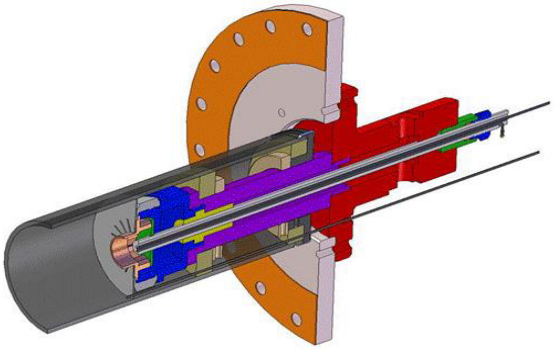

Fig. 1. Drawing of Generic Swirl Burner.

Two hundred OH* chemiluminescense images were taken at 10 Hz at each test condition using Dantec's DynamicStudio software, while the image intensifier gain was controlled via remote control. All images were taken through the top window of the HPOC at a 90° angle to the direction of flow.

Two pieces of equipment were used to characterise the produced emissions. The first is an integrated system developed by Signal Instruments comprising several analyzers: a Flame Ionisation Detector (FID) is employed within a Signal 3000HM to detect total Hydrocarbons (THCs); a heated vacuum chemiluminescence analyser (Signal 4000VM, spanned to 900ppm $C_3H_8$ equivalent) to quantify $NO_x$ concentrations, calibrated to 37.1 ppm NO and 1.9 ppm $NO_2$ ; a multi-gas analyser (Signal MGA), containing an infrared cell for measurement of CO (calibrated for 0-900 ppm) and $CO_2$ (0-9%), in addition to a paramagnetic $O_2$ sensor (up to 22.5%). A new system has been purchased for quantifying trace concentrations of $NH_3$ in the flue gas, and forms a subsystem to the 4000VM NOx analyser. However, this will not be ready until mid-autumn. The second system is a standalone Rosemount NGA 2000 multi-gas analyser, and provides secondary readings of CO, $CO_2$ and $O_2$ all calibrated to the same concentrations previously stated.

*2.2. Numerical studies*

Equilibrium calculations were obtained in order to evaluate all different blends using the software GASEQ. GASEQ is software written in Visual Basic 3 for combustion equilibrium calculations of different types of problem. The fundamentals of the program are based on the complex, balanced chemical calculations defined by Sanford Gordon and Bonnied J. McBridge for NASA [8].

## 3. Experiments and Discussion

*3.1. Test parameters*

A reference flame using methane was first obtained and characterized. In order to increase the ammonia concentration, trials were conducted using air and methane, the latter being slowly reduced whilst the ammonia was increased. Initially an attempt was made to reach 100% ammonia combustion; however, the flame blew off before reaching stable conditions. Concentrations are represented here by volume and similarly, 90%$NH_3$ -10%$CH_4$ concentrations did not provide any results. It was at 80%$NH_3$ -20%$CH_4$ and 66%$NH_3$ -33%$CH_4$ concentrations that quasi-stable flames were obtained.

Based on the observations from a short constant volume bomb study conducted at the GTRC, investigating the burning rate of $NH_3$ -$H_2$ blends it was found that a hydrogen concentration close to 50% would produce similar laminar burning flame velocities to that of methane. Therefore, a 50%$NH_3$ -50%$H_2$ blend was also characterized. All test conditions are presented in Table 1.

Table 1. Parameters defined for the text matrix

| MASS $NH_3$ [g/s] | MASS $CH_4$ /$H_2$ [g/s] | MASS $O_2$ [g/s] | MASS AIR [g/s] | Base POWER [KW] | STOICHIOMETRY |
|---|---|---|---|---|---|
| Ammonia 80%, Methane 20% | | | | | |
| 0.800 | 0.236 | 2.092 | 9.472 | 30.977 | 0.900 |
| 0.800 | 0.236 | 1.883 | 8.525 | 30.977 | 1.000 |
| 0.800 | 0.236 | 1.552 | 7.026 | 30.977 | 1.213 |
| Ammonia 66%, Methane 33% | | | | | |
| 0.584 | 0.340 | 2.592 | 11.733 | 31.840 | 0.740 |
| 0.580 | 0.340 | 2.096 | 9.570 | 31.750 | 0.910 |
| 0.585 | 0.350 | 1.733 | 7.843 | 32.413 | 1.108 |
| 0.578 | 0.340 | 1.666 | 7.540 | 31.705 | 1.143 |
| 0.582 | 0.350 | 1.561 | 7.065 | 32.345 | 1.220 |
| 0.578 | 0.340 | 1.491 | 6.749 | 31.705 | 1.277 |
| Ammonia 50%, Hydrogen 50% | | | | | |
| 0.800 | 0.094 | 4.432 | 19.021 | 31.349 | 0.425 |
| 0.800 | 0.094 | 4.218 | 18.101 | 31.349 | 0.446 |
| 0.800 | 0.094 | 3.998 | 17.160 | 31.349 | 0.471 |
| 0.800 | 0.094 | 3.504 | 15.038 | 31.349 | 0.537 |
| 0.800 | 0.094 | 3.262 | 14.001 | 31.349 | 0.577 |

### *3.2. Results*

It was observed from experimental trials with the generic burner that the flame would present different stabilization patterns based on equivalence ratio. As was predicted the methane flame presented a very stable profile with coherent emissions, showing an increase of NOx and CO at higher equivalence ratios, with peak combustor exhaust temperatures close to an equivalence ratio of 1. In the case of ammonia and methane, it was observed that at lean conditions with an equivalence ratio ~ 0.7, the methane appeared to be burning efficiently at the root of the flame near the exit of the burner with ammonia burning less efficiently downstream.Evidence to support this hypothesis was found in the gas analysis which measured high levels of NOx, but low levels of CO and THCs for this condition. It is believed that the unburnt ammonia was being converted and measured as NOx in the NOx analyser. However, at equivalence ratios greater than 1.0, the flame started to show a shift in behaviour and shape, probably as a consequence of a combined effect between the reduction of oxygen and greater dilution of the methane in the total concentration.

This was evident at an equivalence ratio of 1.05 at which point the flame appears to be incapable of burning both molecules efficiently. NOx emissions start to reduce, with a considerable decrease in $O_2$ , but with increasing CO in the exhaust gases. At this point, the flame starts to show significant signs of thermoacoustics instabilities most likely caused by the slow, uneven reaction of the blend. A stable orange flame was observed at an equivalence ratio of 1.1 probably as a consequence of a high content of $NH_2$ radicals [9], Fig. 2. As the air flowrate was decreased, the flame started to become more unstable with NOx emissions dropping considerably with a reduction in combustion exhaust temperatures of 60°C when compared to the hottest conditions measured close to an equivalence ratio of 1.0. Unburnt hydrocarbons increased substantially in the range of thousands of ppm with the flame showing considerable corrugation at this condition. Due to the reduced bulk volumetric flow rate through the burner the system started to experience flashback. This phenomenon was particularly interesting, since flashback would occur and then the flame would re-position itself at the outlet of the nozzle after a few seconds. This is probably caused due to the different burning rates of ammonia and methane.

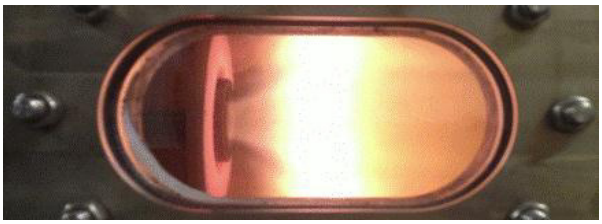

Fig. 2. Flame with an ammonia-methane blend. Equivalence ratio 1.14.

The hydrogen and ammonia blend showed similar trends, but with a narrower band of equivalence ratios where stability occurred. Unfortunately, it proved impossible to operate the burner close to an equivalence ratio of 1.0 due to the relatively low bulk volumetric flowrates used and high $H_2$ content. The flame shape and behavior at the lowest equivalence ratio was very erratic, close to blowoff. Increasing the equivalence ratio was observed to improve flame stability leading to a regime with relatively low emissions ($NO_x$ 220-260ppm). As the equivalence ratio was increased further, combustion remained close to the burner exit nozzle with a very intense hydrogen flame and what appeared to be reasonable $NH_3$ combustion downstream. Emissions showed the highest NOx values (~4500ppm) at 0.577 equivalence ratio before flashing back into the burner.

Chemiluminescense showed clear OH reactions in the methane base flame. When compared to the $NH_3$ -$CH_4$ case, the results denoted much less OH, a phenomenon that was thought to be a consequence of the lower reaction of the molecules and increase of the CH radicals in the process. However, it was surprising that the $NH_3$-$H_2$ process showed a reduced, more uniform OH production when compared to pure methane. It is believed that the cause of this behavior is the increase of $NH_2$ reactions that not only produce an orange flame and block the OH emission, but will also consume NOx as presented by Tian et al [10]. Also, ammonia will decrease the reactivity of hydrogen due to its high concentration allowing a better mixing due to higher residence times. This process will decrease emissions, limit temperatures and stabilize the flame. This concords with other studies (to be published) where Lewis number varies as a consequence of changes in mass-thermal diffusivity. Nevertheless, the experiments show the high 3-Dimensionality of the flame, Fig 3, requiring phase locking at higher repetition rates in the near future.

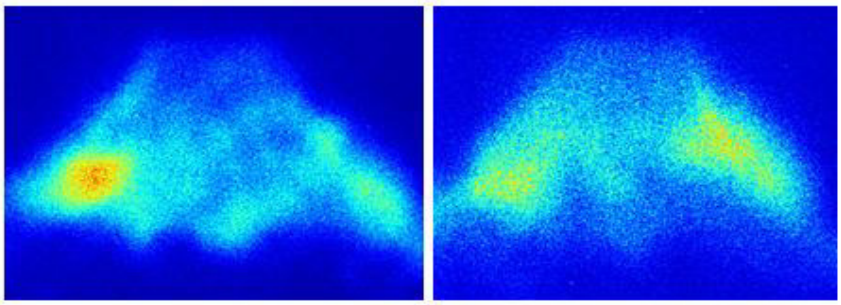

Fig. 3. Instantaneous chemiluminescense comparison between pure methane and hydrogen/ammonia, respectively.

Numerical values showed a very good correlation to experimental measurements, Fig 4. Only CO, $O_2$ and NOx are documented here, but values for other molecules such as $H_2$ , UHC, $CO_2$ , $NH_3$ , etc. were also obtained. Of special interest are those regions after stoichiometry where best stability seems to be obtained. The low amount of emissions, high temperature and good combustion profiles will allow the development of an efficient combustion process close to this point. However, as previously seen in the experiments, it is just a narrow range before the flame starts to vibrate through a thermoacoustic process, meaning that care is required to avoid these unstable conditions.

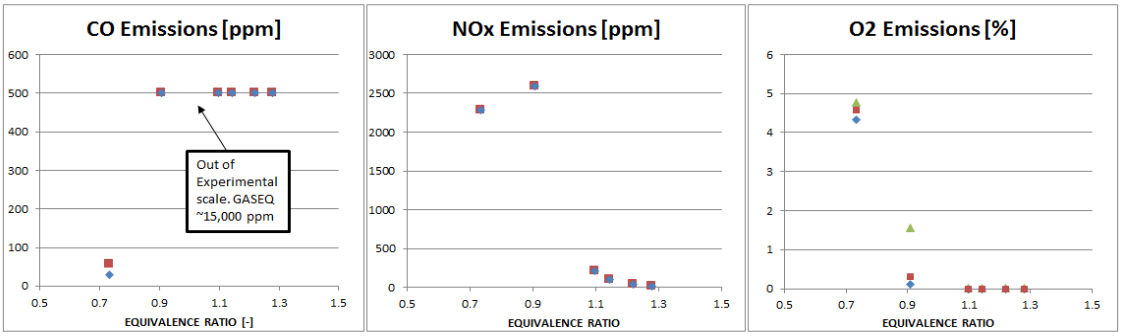


Fig. 4. Results using GASEQ (red symbol) and Emission analyzers (blue and green symbols). Very good correlation was obtained.

## 4. Conclusions

It has been shown that stable flames can be achieved with low emissions using strong swirling flows with both $CH_4$ -$NH_3$ and $H_2$ -$NH_3$ blends. Good correlation exists with experiments and numerical calculations. OH radical emissivity seems to be overwhelmed by other radicals, i.e. $NH_2$ molecules that keep reacting with NOx emissions. It is recognized that there is only a narrow equivalence ratio where high stability, low emissions and high temperature can be achieved, leaving a vast field of research on how to improve these parameters to obtain wider operational ranges.

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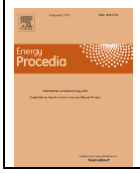


### Biography

Dr. Agustin Valera-Medina is a Chartered Engineer, Lecturer at Cardiff University. He works at the Gas Turbine Research Centre on topics such as combustion hydrodynamics, fluid mechanics, alternative fuels and novel power generation cycles.